In Situ Time-Resolved Diffraction with High Energy X-rays from Metal Oxides: Rietveld Refinements

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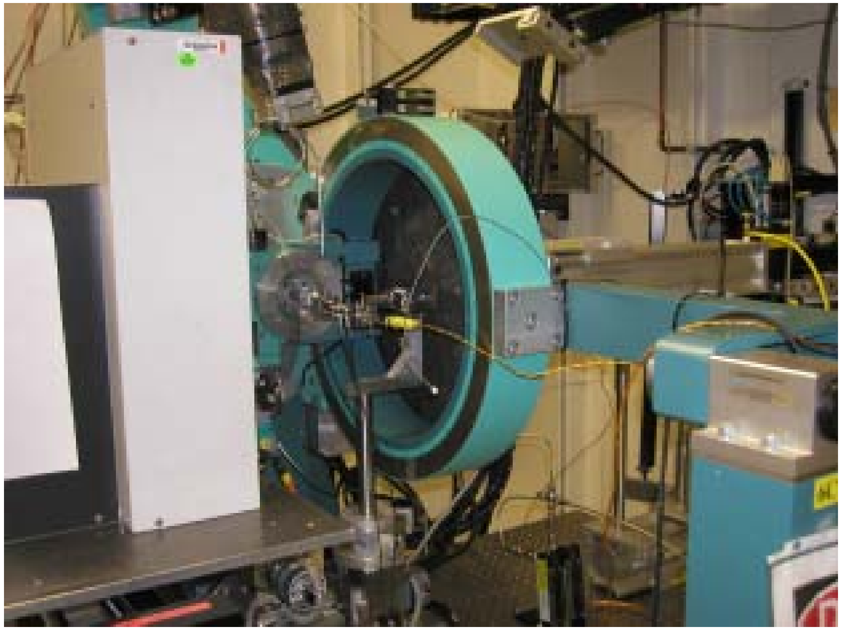
Outline

- Motivation: Structural models of intermediates during catalytic processes
- Technique: In situ Time-resolved XRD
- Applications
  - NiO reduction
  - $CuO/Cu_2O/Cu$ reduction
  - Ceria reduction

Setup for In situ Data Collection

Mar345 Image Plate Detector / Goniometer

Flow Cell

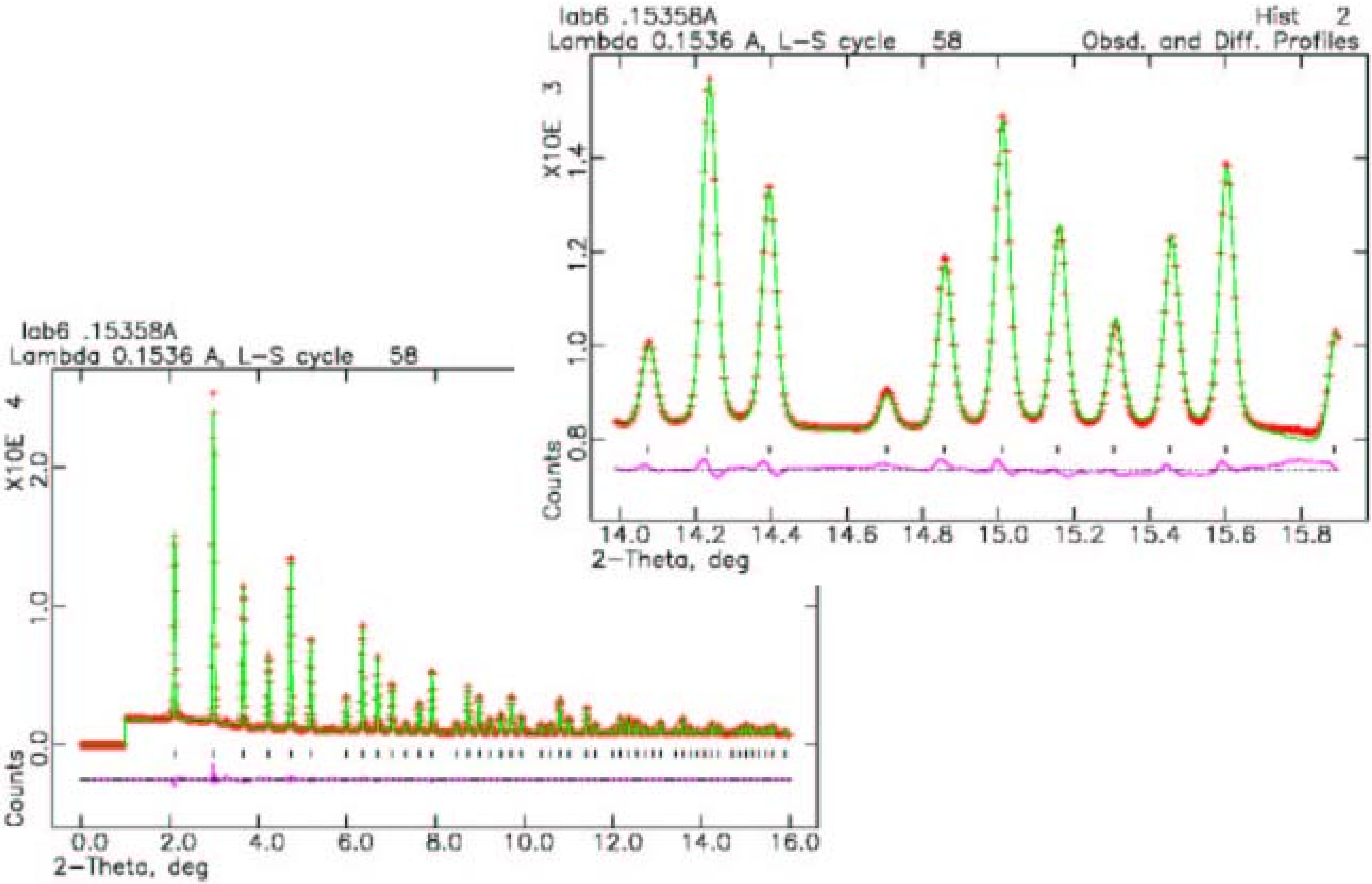


T: 25-950°C P: .001- 120 atm Time: Current=2min/Future 0.1sec

Advantages of Diffraction with High Energy (80-100Kev)

- Low absorption:
  - Corrections negligible
  - Bulk vs. surface properties
  - More penetration of *in situ* cell
- High Q resolution
  - Improved over-determination
  - Reduce U / occupancy correlation

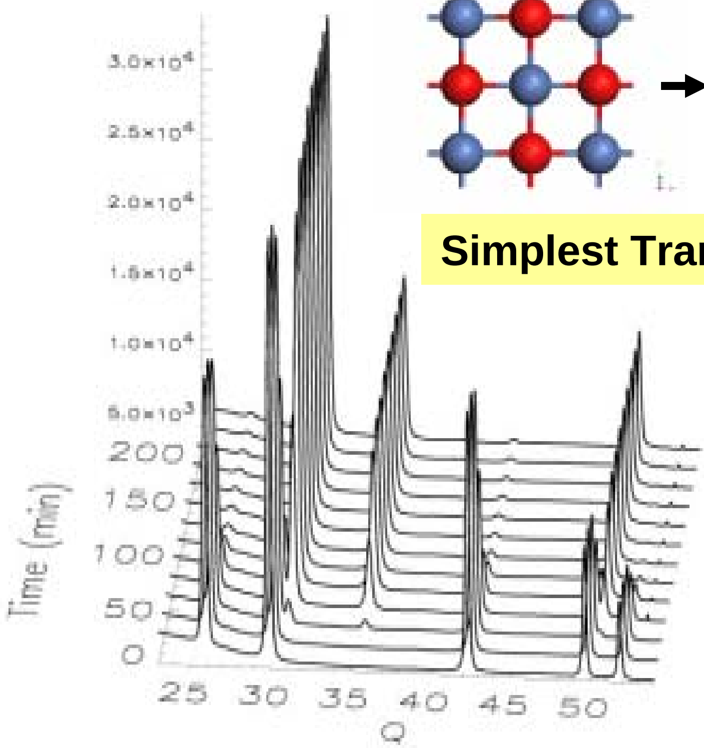
Sharp lines from standard LaB_6

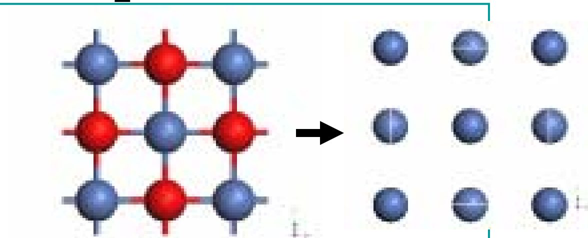


Kinetics NiO Reduction From TR XRD

Isothermal TR-XRD at280°C

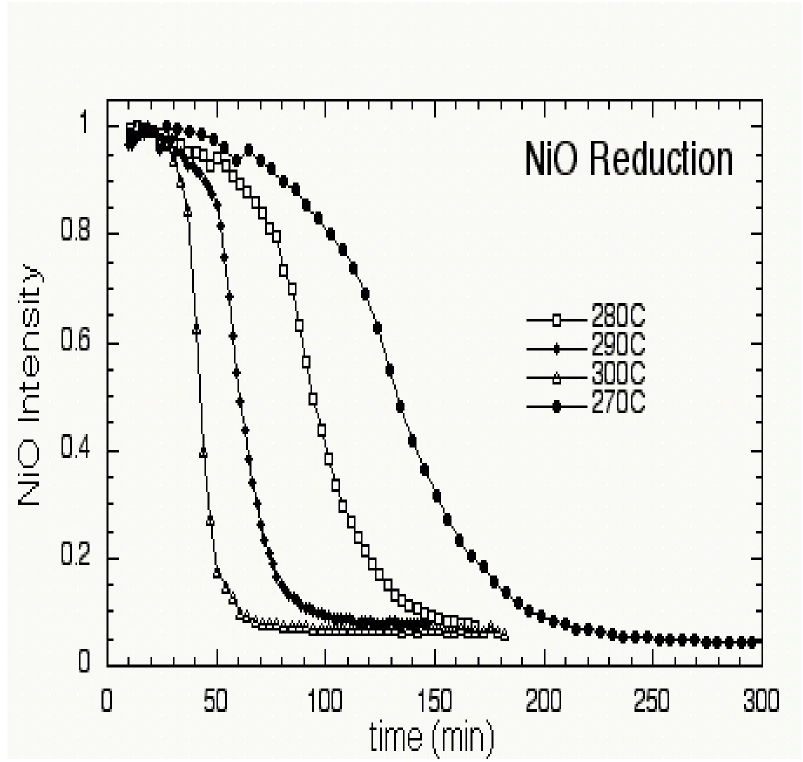
$NiO + H_2 \rightarrow Ni + H_2O$





Simplest Transformation

111 intensity during reduction at four temperatures.



J. Am. Chem. Soc. **124,**346-354 (2002)

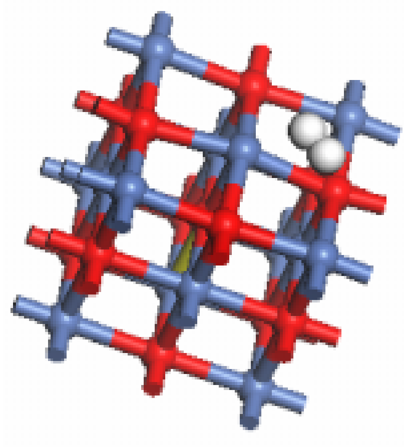
DF Calculations H_2 Interactions with NiO

H_2 on smooth NiO

Weak adsorption

16Kcal/mol barrier

Endothermic



E
N
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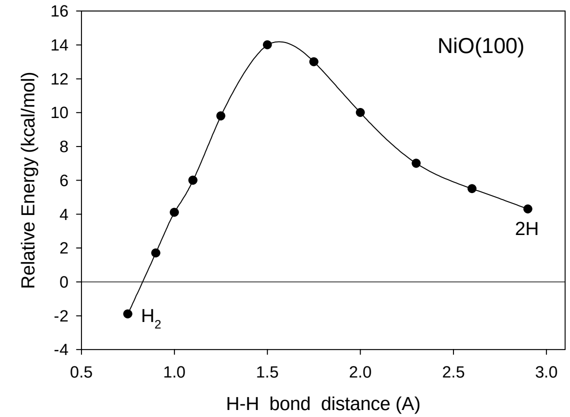


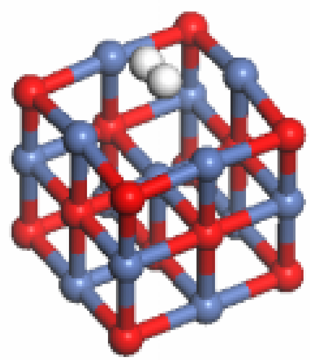
H-H Distance

H_2 on NiO defect

Strong adsorption

8 Kcal/mol barrier

Exothermic



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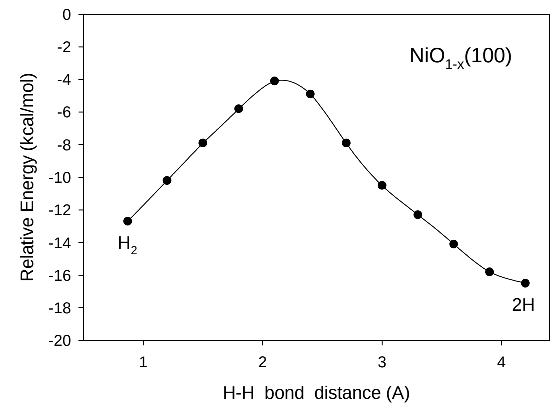
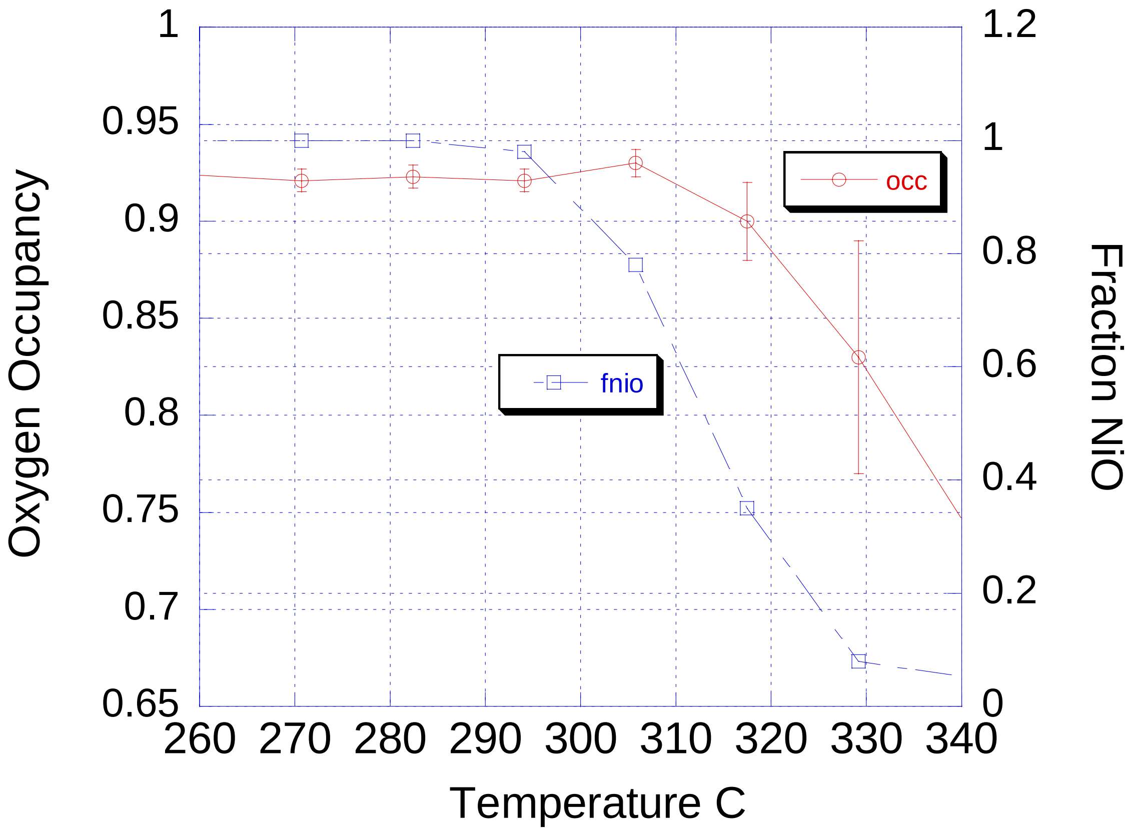


Challenge

- Can refinement of high Q powder data give information about oxygen vacancy and interstitial oxygen formation?
- Can structural information can be obtained?

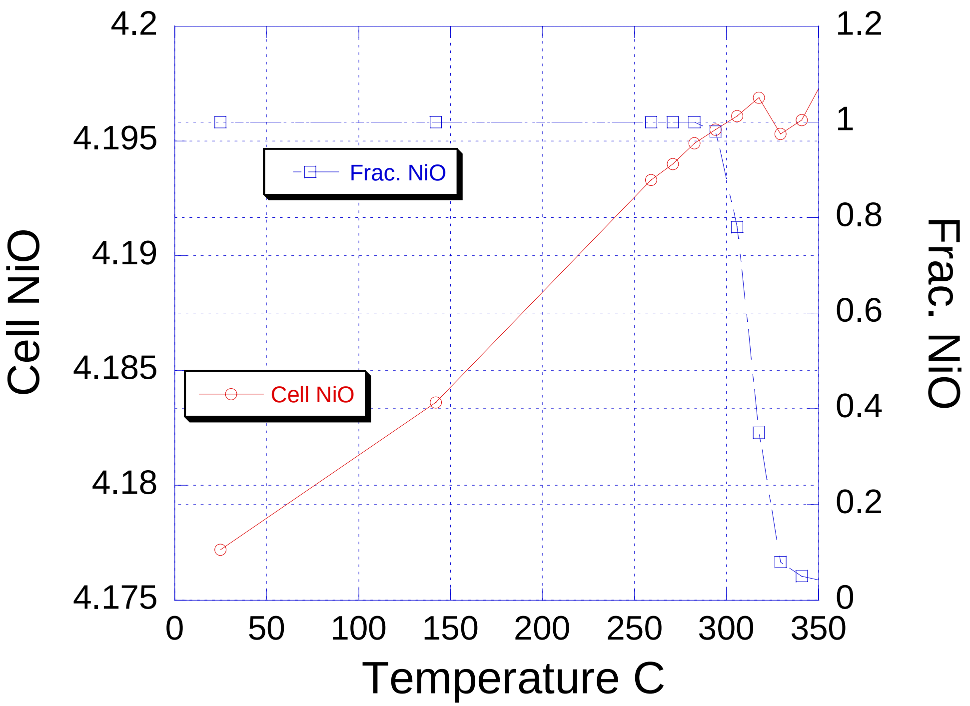
Ramp NiO in 5%H_2/He



1.Fraction NiO decreases faster than oxygen occupancy

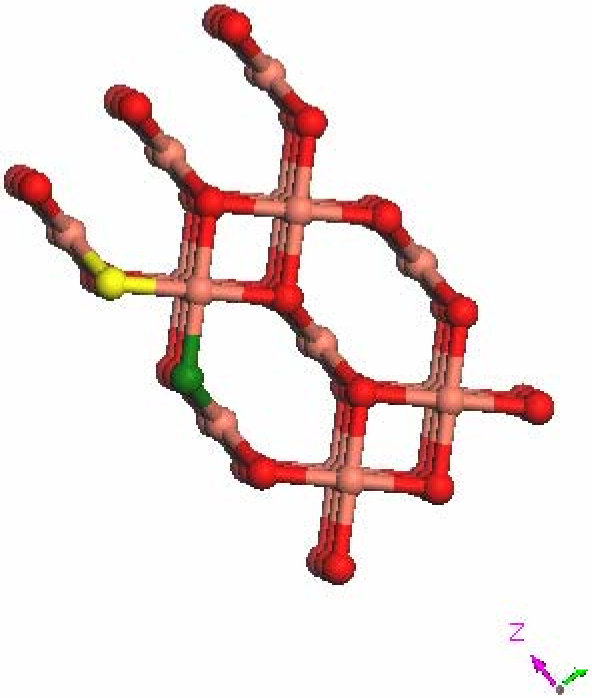
2. Occupancies of oxygen are constant, but slightly low until NiO fraction is less than 0.5

Ramp NiO in 5%H_2/He

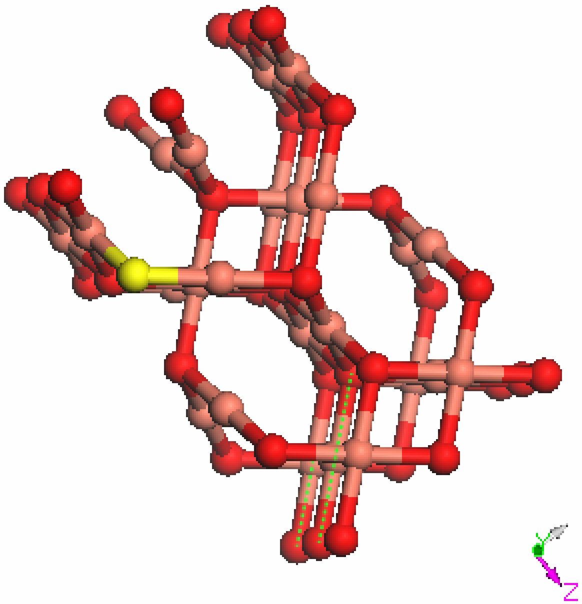


Cell continues to expand until NiO fraction less than 0.4 and then it contracts slightly

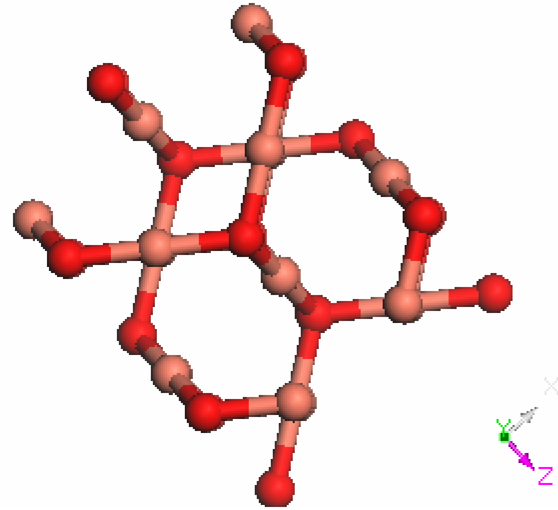
3 Oxides of Copper related to tetragonal cell show common features/O changes



CuO



Cu_4O_3

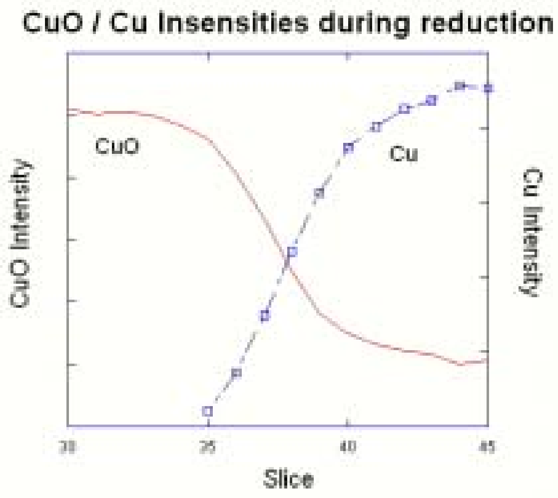


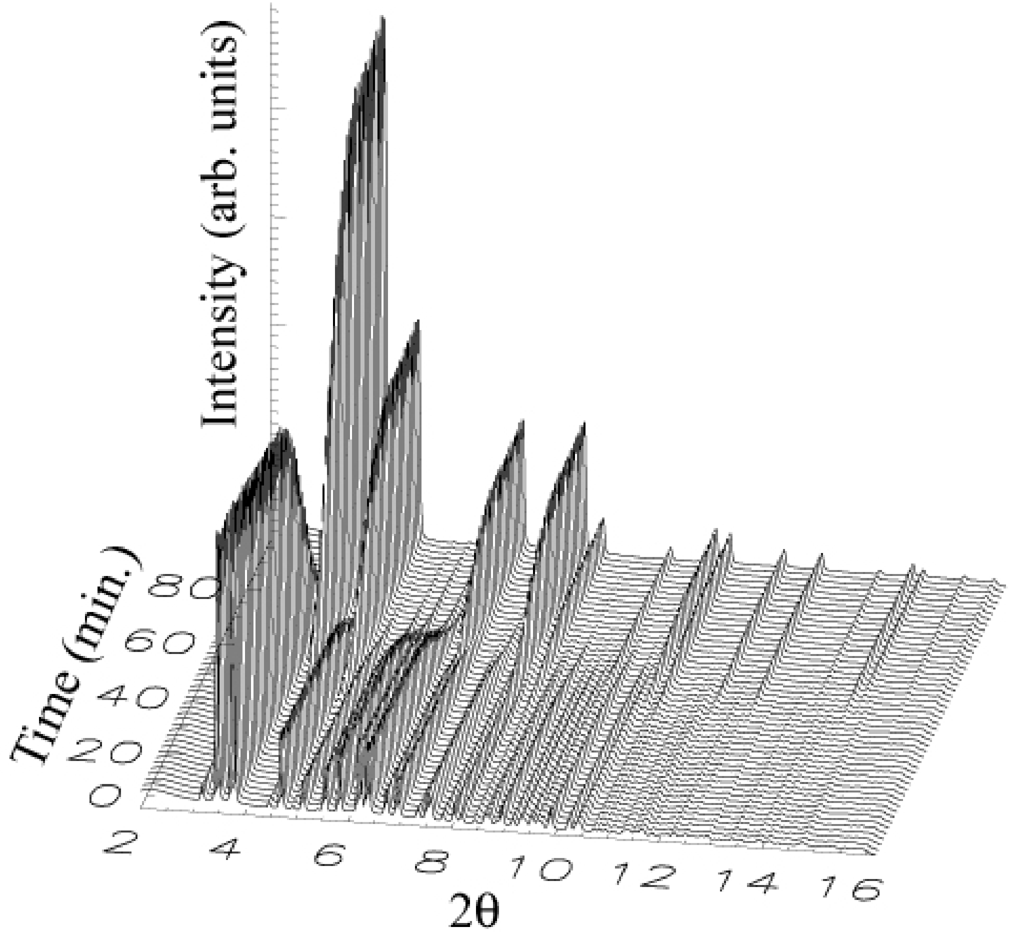
Cu_2O

- O

- O

Time resolved diffraction pattern

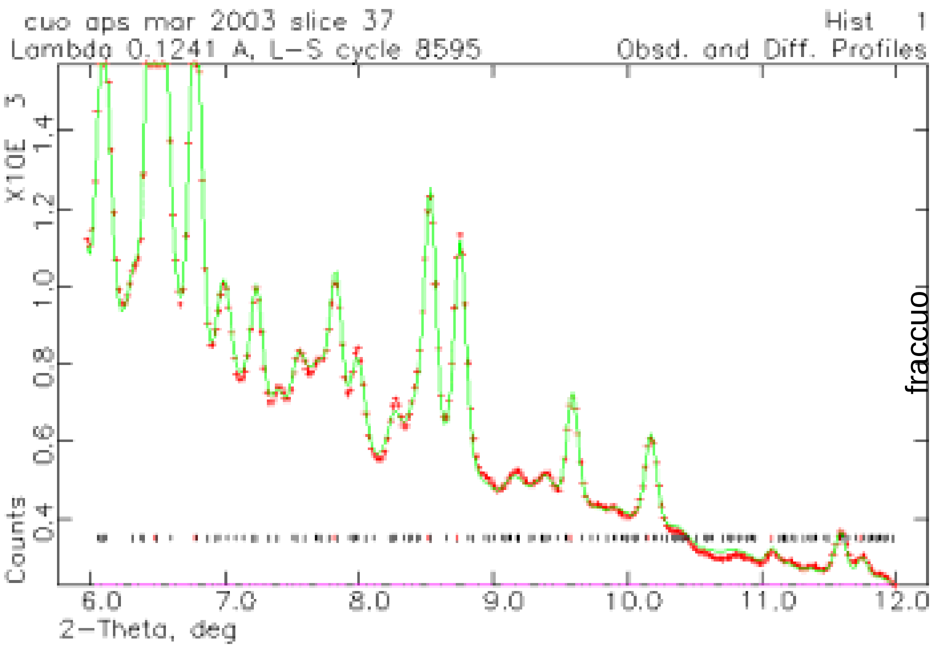


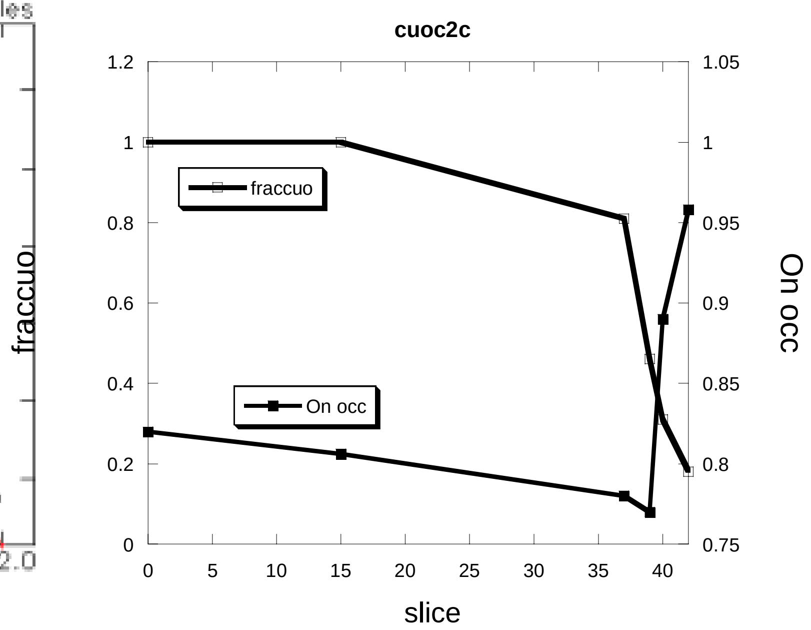


No diffraction from
Intermediate phases
Is there any information
In the TR intensity data
of CuO phase?

Can you refine O occupancies when small weight fraction?

Current approach fails at weight fraction <0.46

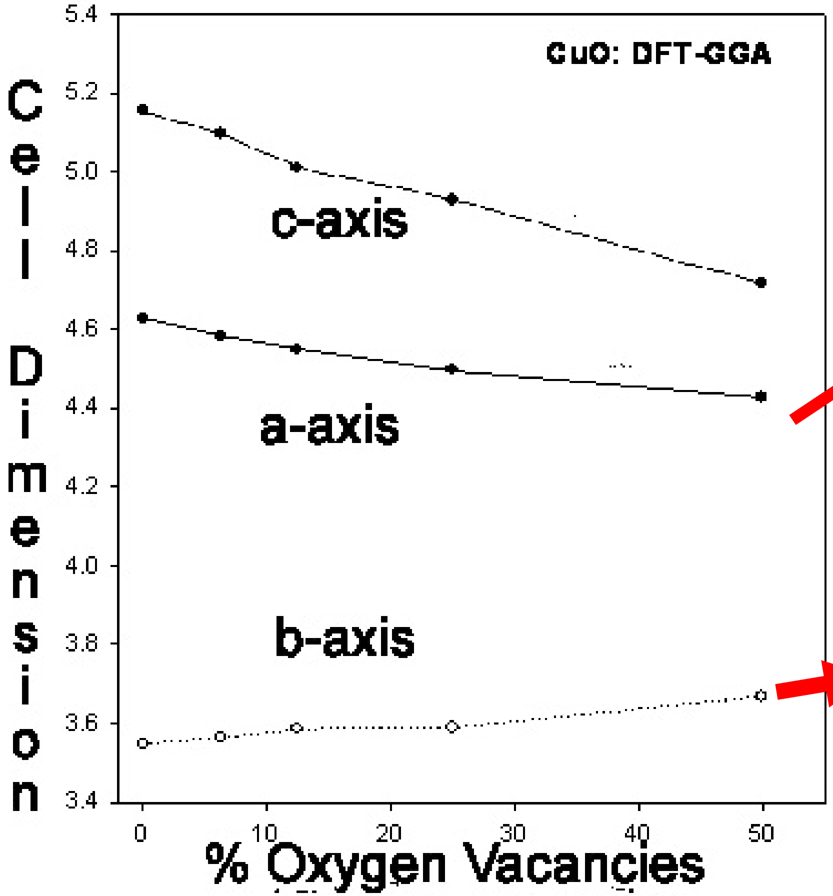


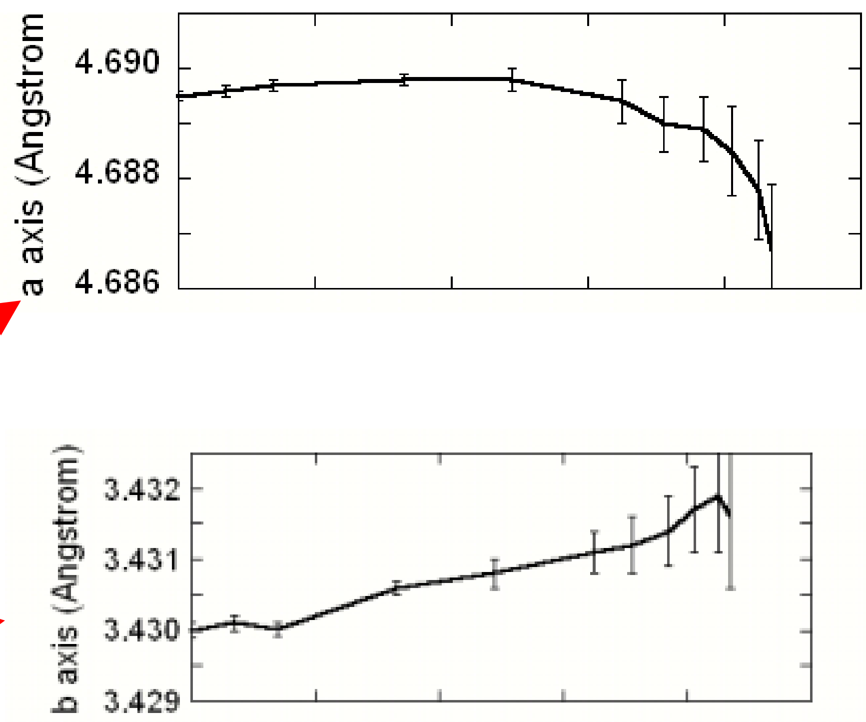


Observed and Calculated Effect of Oxygen Vacancies on Cell Dimensions

calculated

X-ray





Wt Fraction Cu

Kim, J, et al J. Am. Chem. Soc. (2003) **125**, 10694

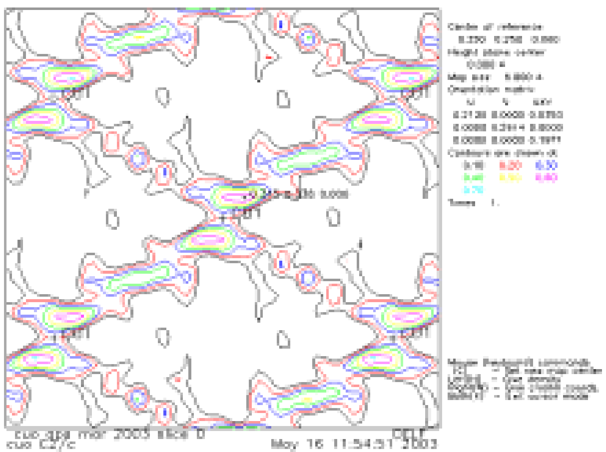
Gsas refinement of initial CuO

Thermal	O occ	$R(F^2)$	χ^2
Aniso Cu	0.820(6)	0.029	0.37
aniso Cu	1.0(fix)	0.036	0.62
Iso Cu	0.828(6)	0.034	0.50
Iso Cu	1.0(fix)	0.039	0.84

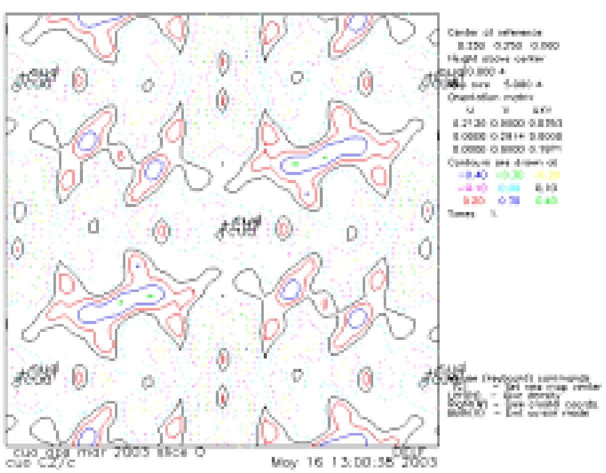
O Occupancy significant, but not full

Cu anisotropic motion significant

Cu disorder
High Q data important to resolve peaks



Cu on 1bar



Cu .08A from 1bar

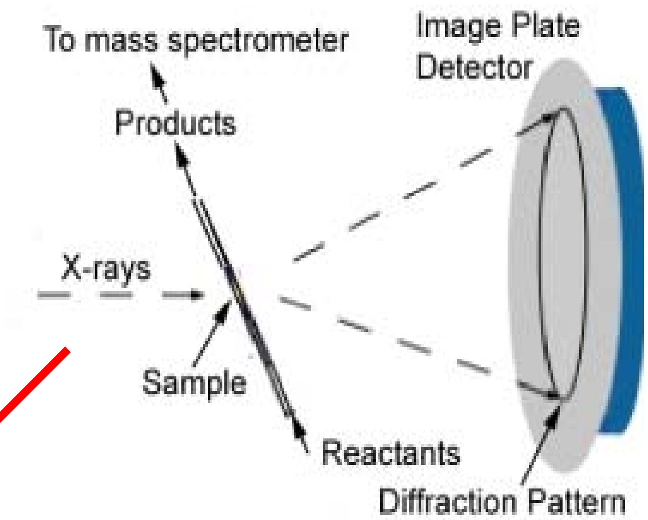
$CuO + H_2 \rightarrow Cu + H_2O$

- Oxygen occupancy change in CuO small until material more than 50% gone
- CuO Cell dimension changes
  - Consistent with H imbedding initially
  - Oxygen vacancies at end
- High Q data reveals Cu disorder

Water Gas Shift Reaction:

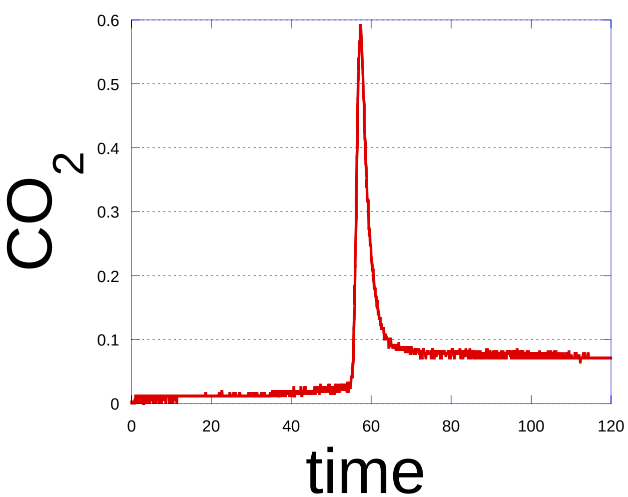
Simultaneous Measurement

$CO + H_2O \rightarrow H_2 + CO_2$

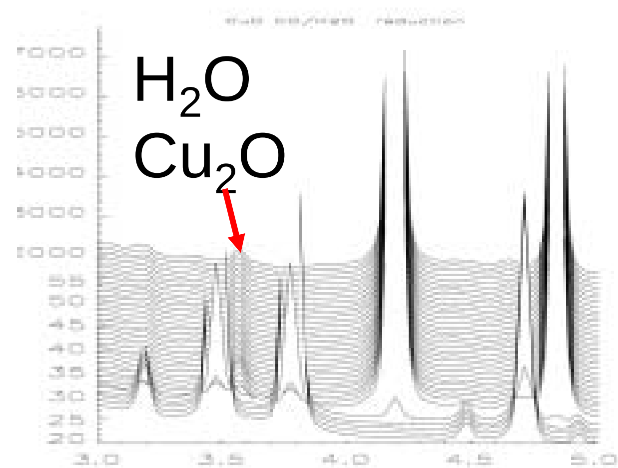


Mass Spectrum

Diffraction Pattern



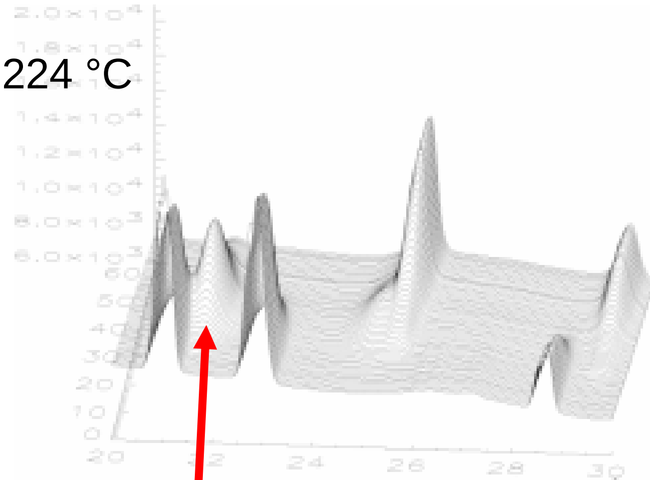
Cu_2O diffraction line observed during catalytic formation of CO_2



Formation of Cu_2O intermediate.

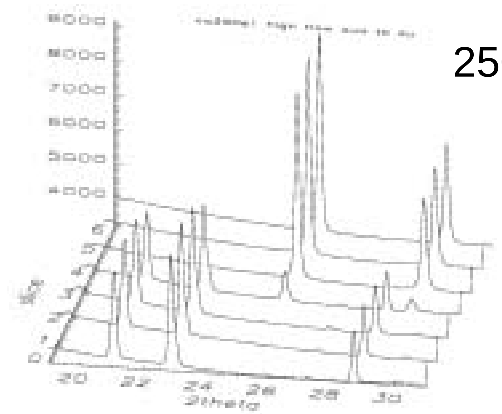
Isothermal reduction with CO

224 °C



lower flow

250 °C



High flow

Equilibrium Cu_2O phase forms at lower flow

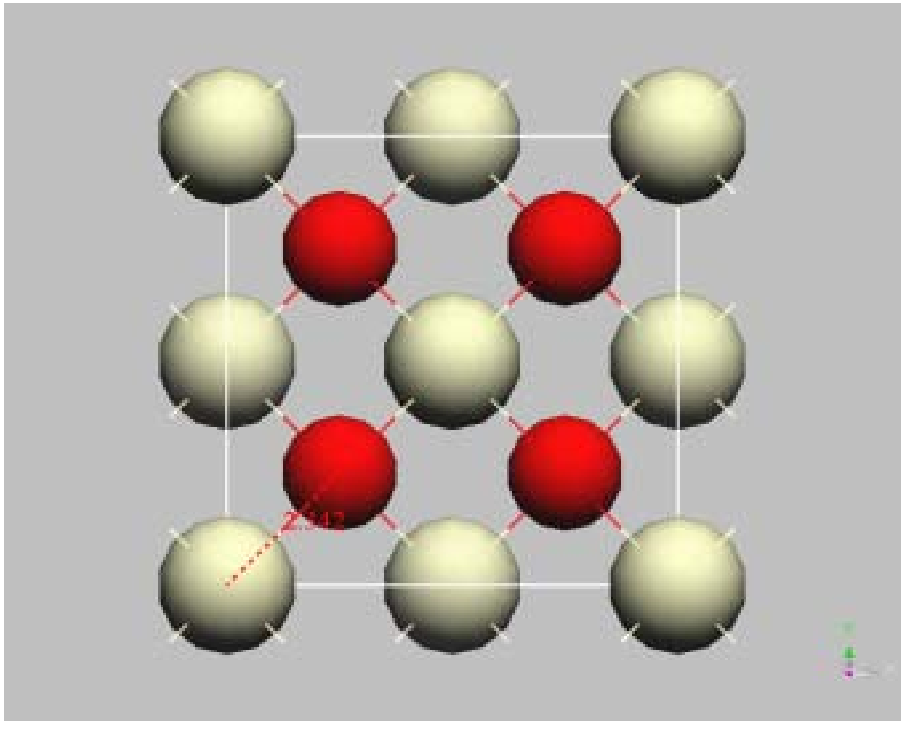
- Meta stable CuO $\rightarrow$Cu before Cu_2O forms in high flow

Refinement shows possible disordered Oxygen in Cu_2O

Wang X, et al J Phys. Chem. (in press)

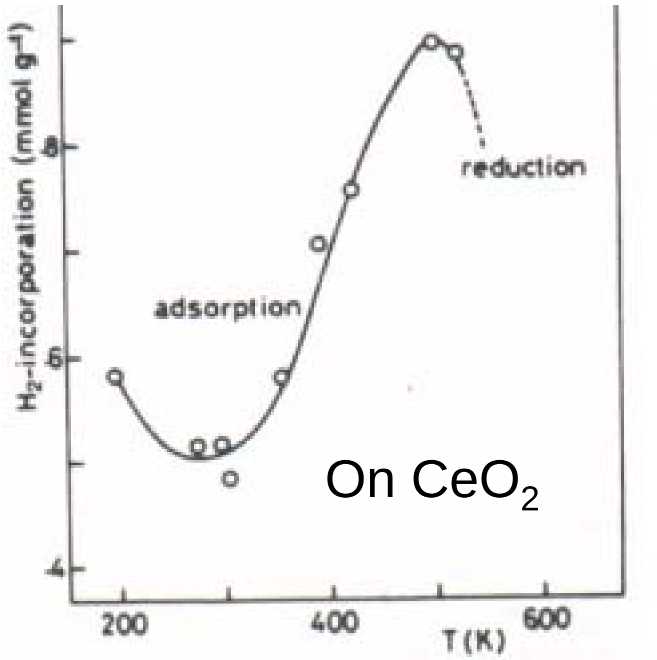
CeO_2

- Important “Oxygen” modulator in catalyst
- Reversible H_2 or CO reduction (<1000C)results in cell expansion but no phase transition.



Previous Experiments Binding H_2 or CO

Fierro, et al **JSSC** (1987)

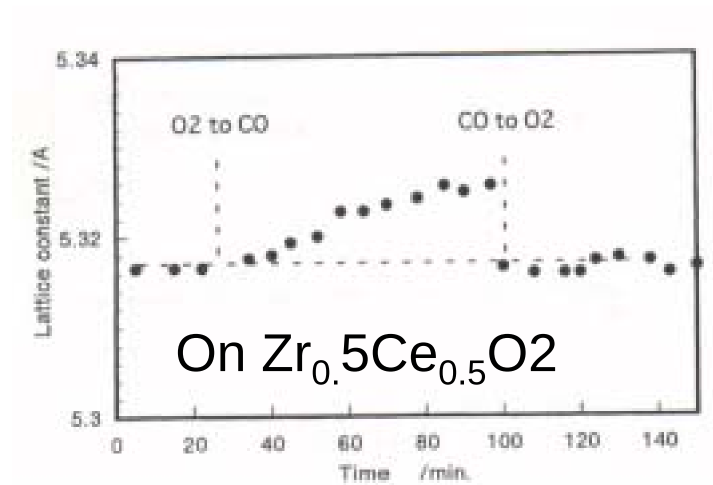


Microgravimetric measurement

Activated process

Reduction above 573°K

Ozawa & Long **Cat.Today** (1999)

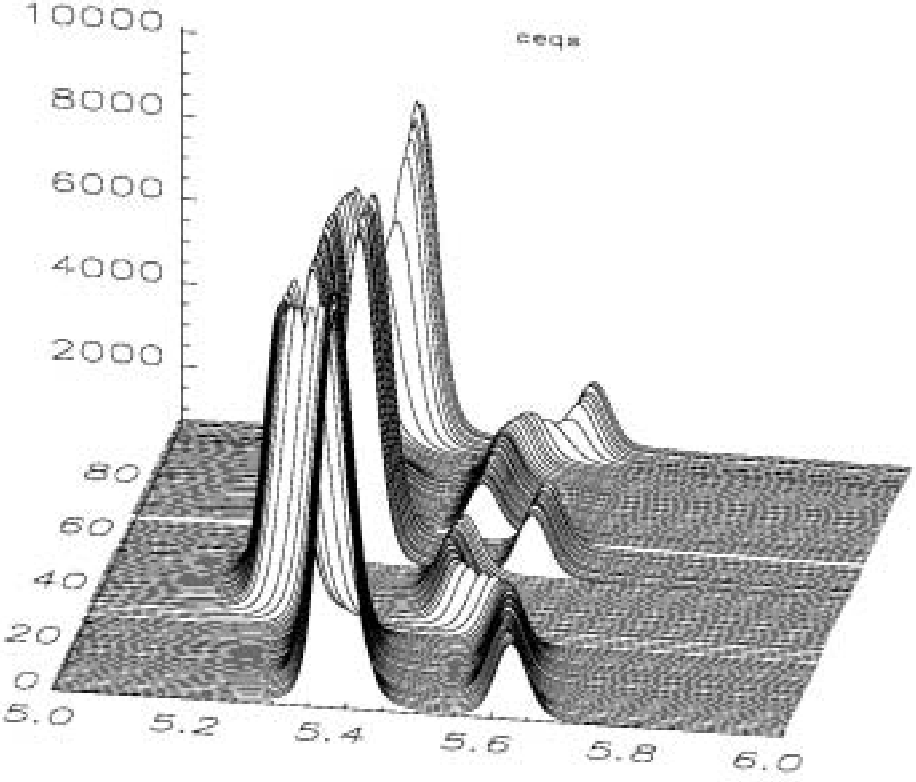


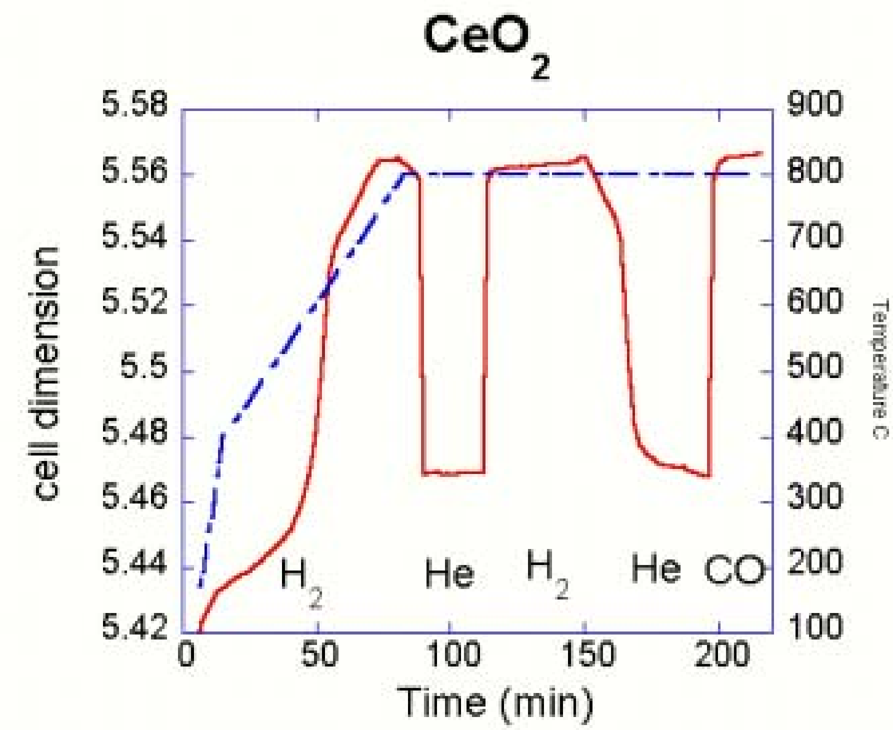
In situ X-ray diffraction at 600°C

Reversible “process”

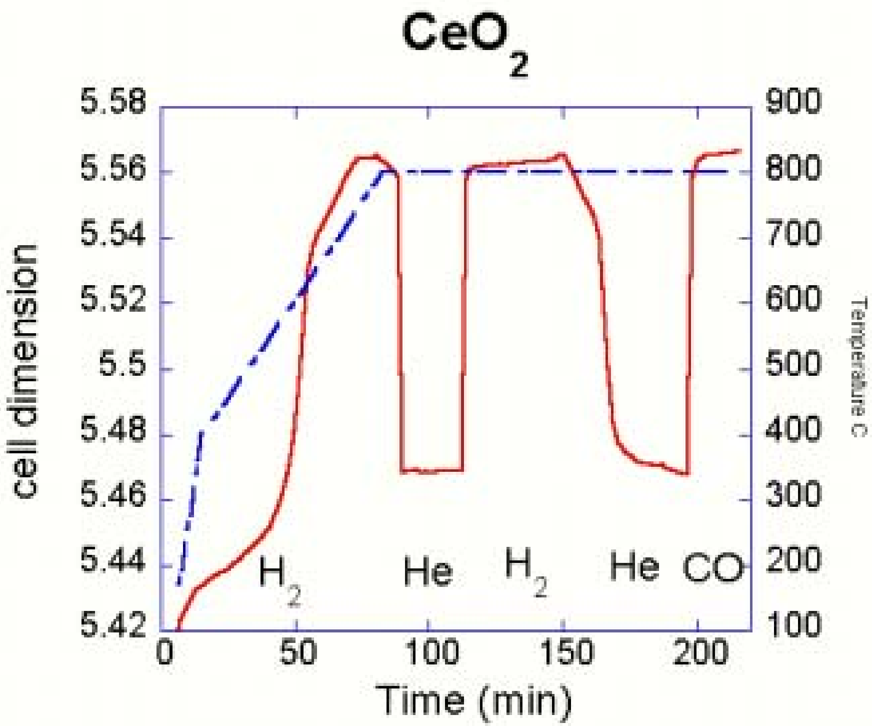
Small cell dimension change

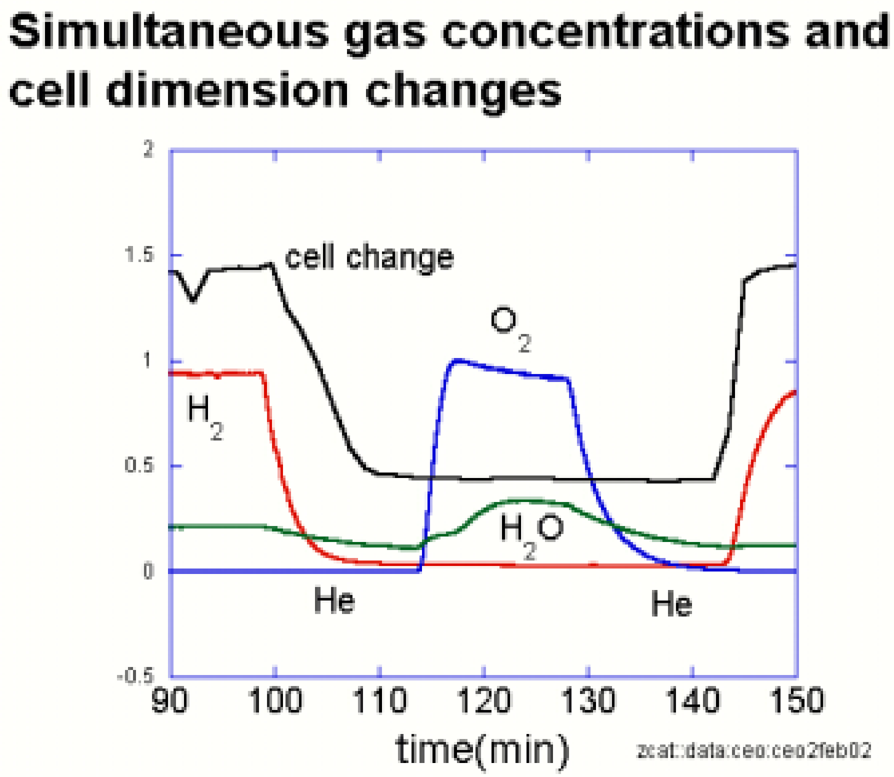
In situ oxidation/reduction of bulk ceria





Cell Expansion In H_2 and CO





- Anomalous cell expansion during heating
- Cell contraction in He
- Cell expansion in CO too

Refinement of Bulk CeO_2 In Situ Data

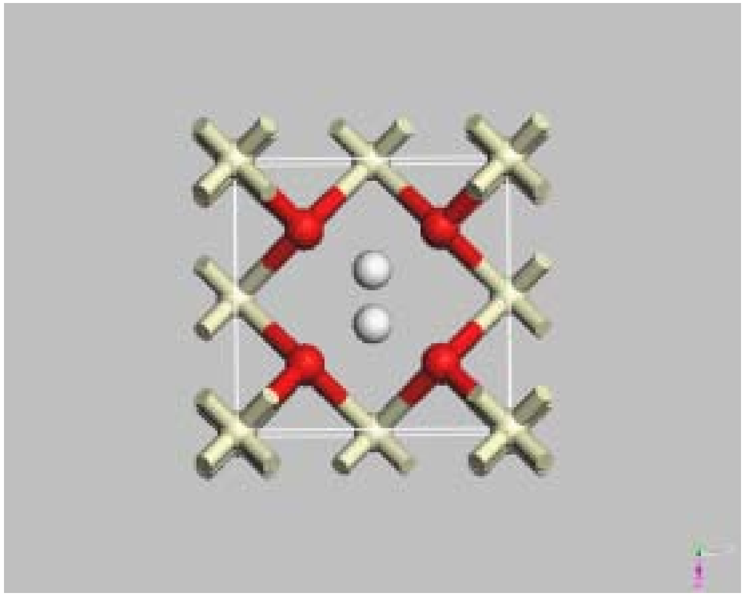
Conditions	dist(CeO)	Occ (O)	χ^2
25°C Air reference	2.342Å	1.00	0.6
800 °C H_2/He	2.409	0.89	0.3
800 °C He only	2.368	1.00	0.3
800 °C CO/He	2.410	0.93	2.7

On reduction at 800 °C

Distance of CeO increases 0.04Å in H_2/CO

Occupancy of O changes 0.1 in “reduced” CeO_x

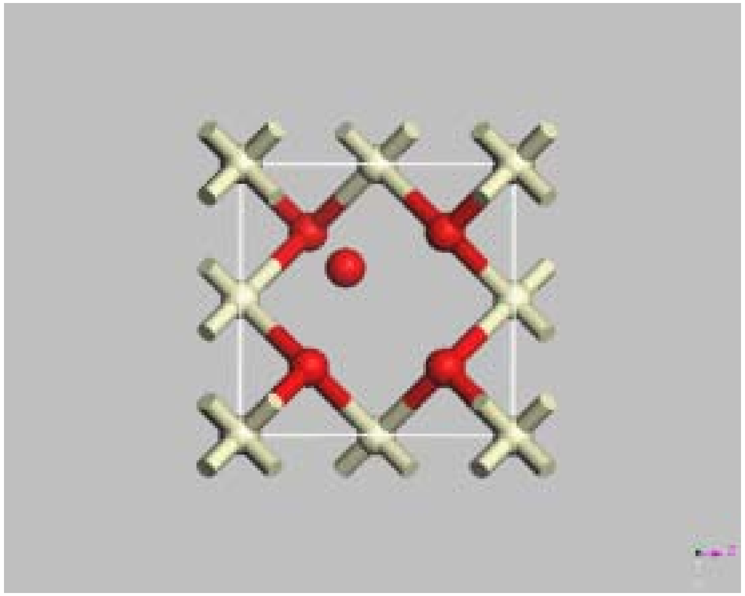
Models in Cavity



H_2

Stable minima in DFT

Density in $\Delta\rho$ map

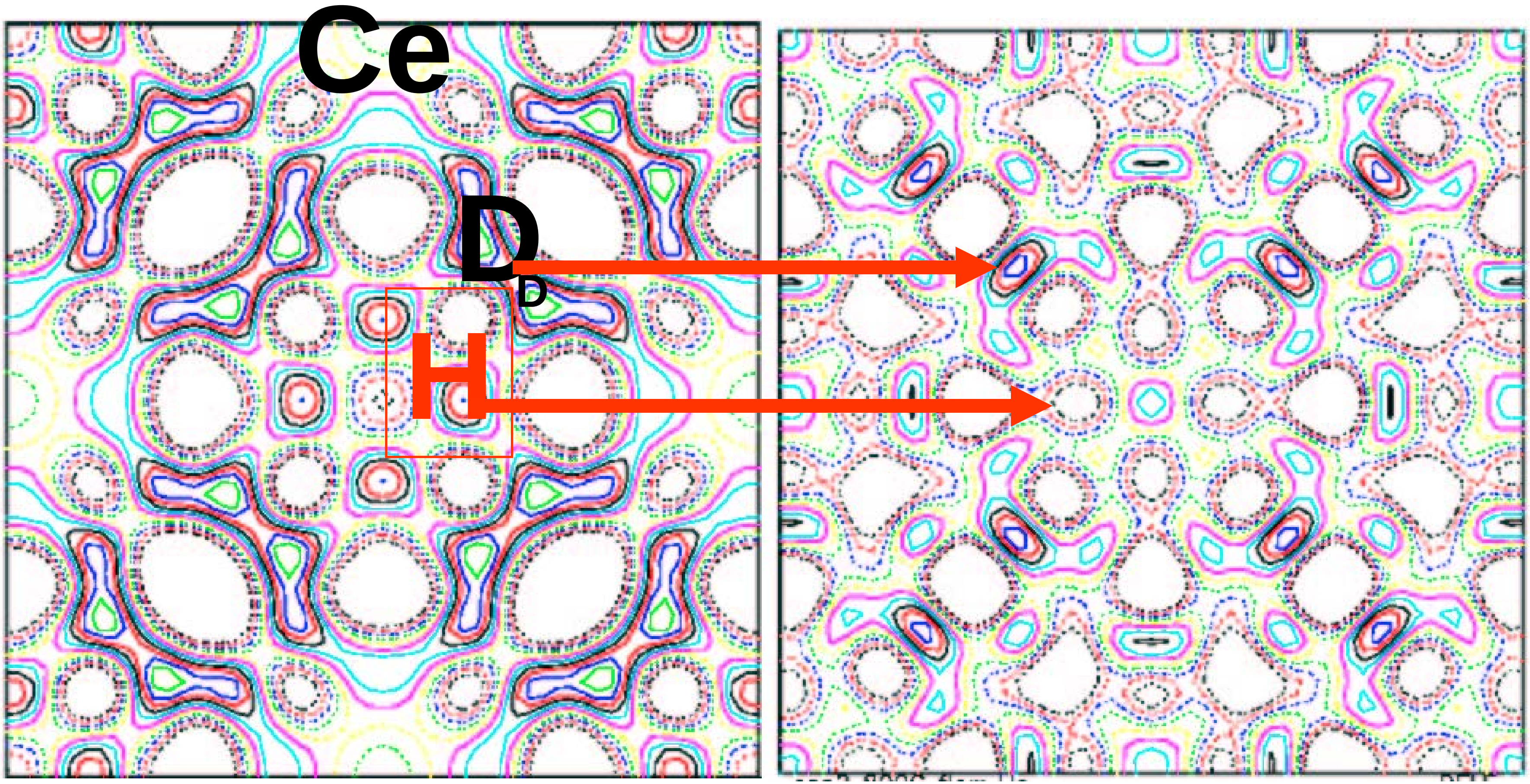


Egami Frenkel Defect

DFT move back to normal site

Density in $\Delta\rho$ map

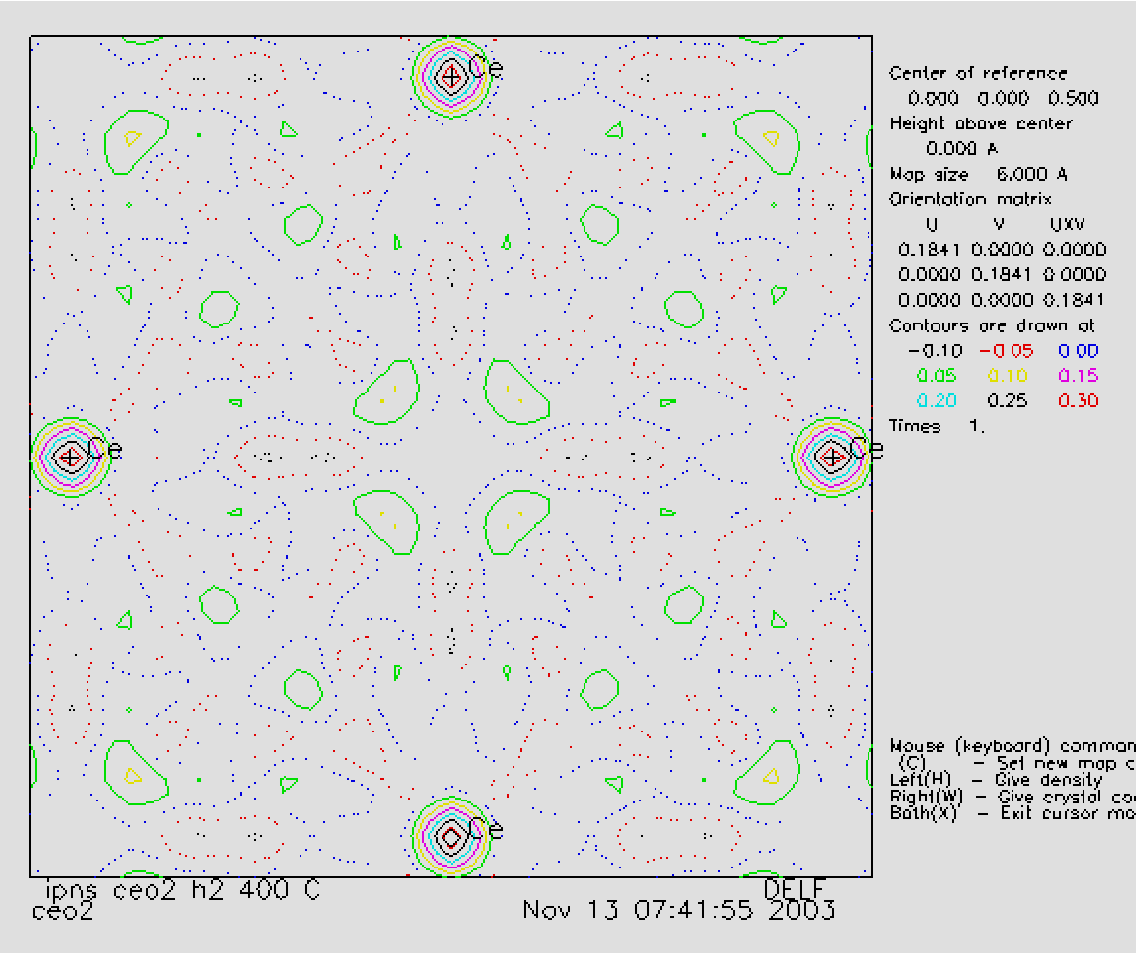
Electron Density in Central Cavity



H_2/He Flow 800 C

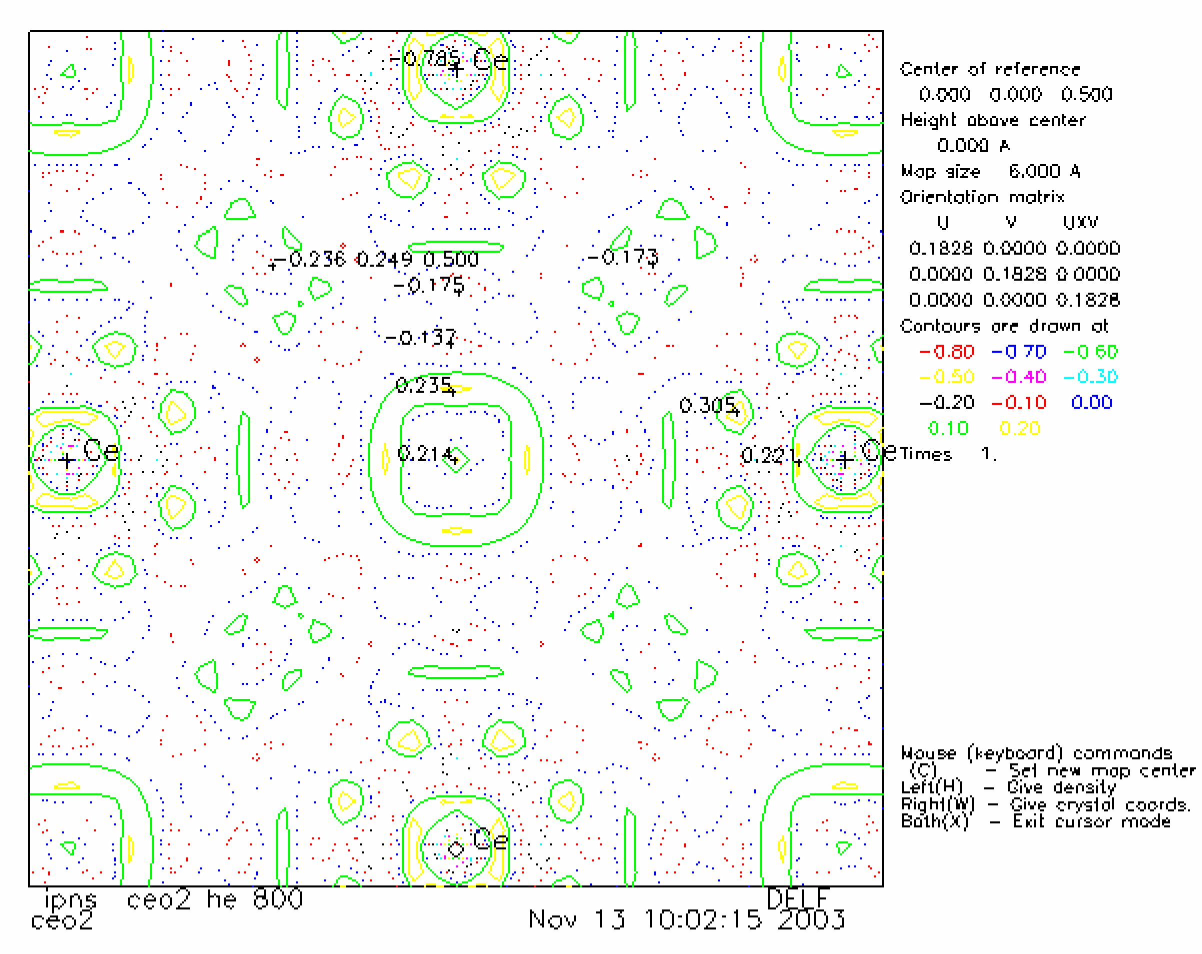
He only Flow 800°C

Neutron diffraction from bulk ceria in H_2 at 400C



Rwp= .16 RFsq= .13 a=5.4327 occ=.956

Neutron diffraction from bulk ceria in H_2 at 400C



pRwp=0.14 RFsq=0.15 a =5.4711occ=.925

Vacancies in Ca doped ceria

Ce:Ca ratio	Lattice Constant	O Occupancy in lattice
1:0	5.420	1.02
9:1	5.416	0.94
8:2	5.416	0.94
2:1	5.394	0.86*

- 0.86 implies $Ce_{0.66}Ca_{0.33}O_{1.72}$ instead of ideal $Ce_{0.66}Ca_{0.33}O_2$
- Rodriguez, et al. J. Phys. Chem. (2003) **119**, 5659-5669

Conclusions

- In situ time resolved powder diffraction provides:
  - Useful information of intermediate phases
  - Faster detector would help
  - Structural information during transformation
    - Complexity of refinement restricts certainty of model
    - Useful trends of transformation can be obtained

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